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Author: M. Detcheberry P. Destrac X-M. Meyer J.-S. Condoret

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Phase equilibria of aqueous solutions of formaldehyde and methanol: improved approach using UNIQUAC coupled to chemical equilibria

M. Detcheberry[a,b], P. Destrac[a,b], X-M. Meyer[a,b], J-S. Condoret[a,b,*]

[a] *Université de Toulouse ; INPT, UPS ; Laboratoire de Génie Chimique ; 4, Allée Emile Monso, F-31030 Toulouse, France*
[b] *CNRS ; Laboratoire de Génie Chimique ; F-31030 Toulouse, France*

Abstract

The study of the phase equilibria involving formaldehyde is still relevant because of its presence in new processes where biomass is the raw material. The coupling between physical phase equilibria and chemical reactions makes its thermodynamic description a challenging task. In this work, an improved approach using UNIQUAC coupled to chemical equilibria was developed and compared with experimental data from the literature. The first application was done for the phase equilibria of the formaldehyde-water system and distribution of oligomers in the liquid phase was computed. The second and the third applications respectively considered the phase equilibria of the formaldehyde-methanol system and the formaldehyde-water-methanol system.

Keywords: phase equilibria, modeling, formaldehyde, water, methanol, UNIQUAC

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1. Introduction

Formaldehyde has been used for long as intermediate chemical in several industrial processes (such as polymers production [1], adhesive synthesis [2], trioxane production [3], formaldehyde distillation [4, 5]...). Because of its acute toxicity (corrosivity, carcinogenicity, mutagenicity and reprotoxicity), its use is declining but studies about systems involving this compound are still relevant either because they are useful for depollution processes [6, 7] or because emerging processes where lignocellulosic biomass is the raw material are likely to generate this compound. This is for instance the case for thermal processes like torrefaction [8, 9] where formaldehyde was shown to be present in large amount in the gaseous effluent alongside other compounds including water and methanol. Because of its specific nature, modeling the behavior of formaldehyde is an important step for understanding and controlling of thermal processes involving lignocellulosic biomasses in general. Indeed, formaldehyde is also present in pyrolysis oils [10] and should be taken into account for depollution processes.

Formaldehyde is the smallest aldehyde molecule and is a gas at ambient conditions. It is highly soluble and reactive in water. Therefore formaldehyde is commonly handled in aqueous and/or methanolic solutions that stabilize it, the most common being known as formalin, an aqueous solution of formaldehyde and methanol containing between 37% and 41% of formaldehyde. Indeed, aqueous solutions of formaldehyde and methanol are not simple ternary systems because formaldehyde reacts with both methanol and water to form diverse polymers. Thus, formaldehyde is not stored or processed as a pure substance. Reactions with water generate methylene glycol, and poly(oxymethylene) glycols. Reactions with methanol form hemiformal and poly(oxymethylene) hemiformals.

This leads to a great complexity for the description of phase equilibria of this system and surprisingly, very few works are present in the literature. The most comprehensive studies originate from the group of Maurer at the University of Kaiserslautern (Kaiserslautern, Germany) and constitute the reference for this domain. Data from this group were used in this work [11, 12, 13, 14, 15, 16, 17, 18]. The model established by this group was used as a basis for our improved approach that was assessed by comparison to experimental data and the original model.

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[*] Corresponding author

Email address: `jeanstephane.condoret@ensiacet.fr` (J-S. Condoret)

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2. Description of the reactive vapor-liquid equilibrium model

As mentioned above, when modeling the thermodynamic behaviour of such systems, the main difficulty is to account for the coupling of chemical and physical equilibria of these reactive molecules. In this work, the physical and the chemical phenomena were implemented in a uncoupled way in the model so as to differenciate the effects of weak intermolecular interactions of the physical equilibria from the strong intermolecular interactions involved in the chemical reactions. For the vapor-liquid equilibrium an heterogeneous approach was adopted: the physical interactions between all species are taken into account through activity coefficients calculation in the liquid phase and through an equation of state for the gas phase. In this study, chemical reaction equilibrium constants are not considered as variables. The only variables to be estimated are the binary interaction parameters. The figure 1 illustrates the outline of this model. Note that the system is described at equilibrium and no kinetic data are introduced in the modeling. Thus, the thermodynamic problem includes both:

- chemical equilibria of the methylene glycol, hemiformal, poly(oxymethylene) glycols, poly(oxymethylene) hemiformals formation.
- physical phase equilibria of water, methanol, formaldehyde, methylene glycol and hemiformal.

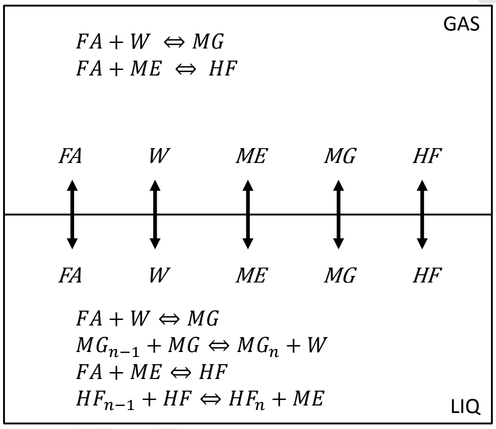
GAS
$FA + W \Leftrightarrow MG$
$FA + ME \Leftrightarrow HF$
FA
W
ME
MG
HF
FA
W
ME
MG
HF
$FA + W \Leftrightarrow MG$
$MG_{n-1} + MG \Leftrightarrow MG_n + W$
$FA + ME \Leftrightarrow HF$
$HF_{n-1} + HF \Leftrightarrow HF_n + ME$
LIQ

Figure 1: Scheme of the vapor-liquid phase and chemical equilibria for aqueous solution of formaldehyde and methanol

This description of phase equilibrium in chemical reactive mixtures was fomerly proposed by Maurer [11] and applied to aqueous solutions of formaldehyde and methanol. The UNIFAC Original model was chosen to represent the physical phase equilibrium. The advantage of the UNIFAC Original method lies in its predictive aspect but an important limitation is the influence of so-called proximity effects which are not accounted for. Indeed, for mixtures containing small molecules, the environment has a strong effect on the phase equilibrium. In this work, chemical description of the Maurer's approach was not modified but thermodynamic approach was improved using the UNIQUAC model. The main interest of the UNIQUAC model is the use of available experimental data for binaries to provide a more realistic description of the mixture behavior and for instance does not suffer from the limitations of UNIFAC Original, such as proximity effect. Moreover, it is able to account for size effects. Note that our approach is intended to be extended to the description of more complex mixtures containing other small polar molecules as encountered in gaseous effluents of wood torrefaction processes. A representative model of the system would allow proposing and designing a reliable separation process. In this case, the sole use of the UNIFAC Original model would give imperfect prediction.

2.1. Chemical reactions in aqueous and methanol formaldehyde solutions

Chemical equilibria are included in the thermodynamic description and chemical equilibrium is assumed. Formaldehyde is a very reactive component. In this model, the prominent reactions were assumed to be:

- formation of methylene glycol (MG): $CH_2O + H_2O \rightleftharpoons HO(CH_2O)H$
- formation of poly(oxymethylene) glycols (MG$_n$): $HO(CH_2O)_{n-1}H + HO(CH_2O)H \rightleftharpoons HO(CH_2O)_nH + H_2O$
- formation of hemiformal (HF): $CH_2O + CH_3OH \rightleftharpoons CH_3O(CH_2O)H$
- formation of poly(oxymethylene) hemiformals (HF$_n$): $CH_3O(CH_2O)_{n-1}H + CH_3O(CH_2O)H \rightleftharpoons CH_3O(CH_2O)_nH + CH_3OH$

The more concentrated the formaldehyde solution, the higher the degree of polymerization (see figure 2). Maurer's works considered polymers up to degree 4. Nevertheless, in this work, to obtain mass balance accuracy better than 5%, it was necessary to consider polymers up to degree 7.

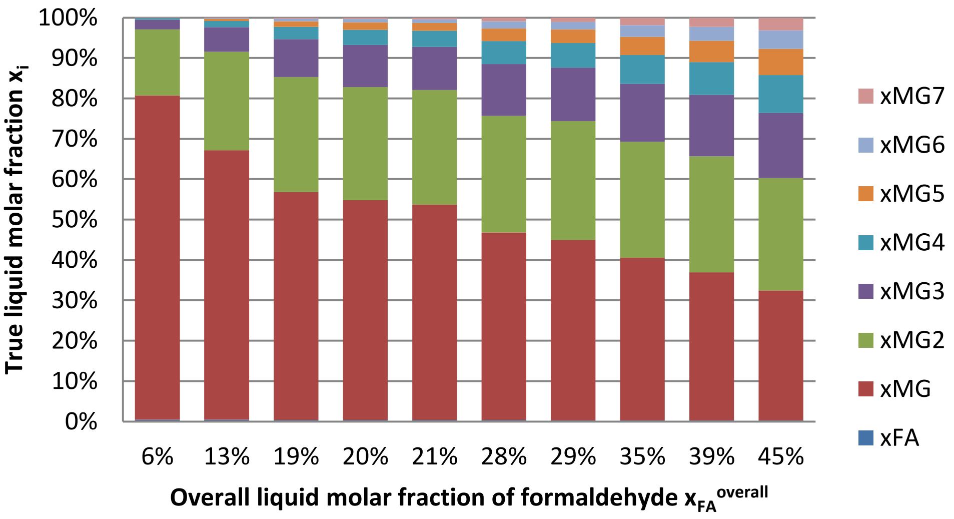

Figure 2: isothermal phase equilibrium for water-formaldehyde system at 353K [17]:species distribution vs overall molar fraction of formaldehyde in the liquid phase

Chemical reaction equilibrium constants are taken from the literature and follow a polynomial law: $\ln K = a_1 + a_2/T$. The coefficients are given in table 1.

2.2. *Description of the liquid phase*

The major improvement proposed in this work is a better description of the thermodynamic behavior of the liquid phase. The physical interactions between all species are taken into account by an empirical approach based on local composition: the universal quasi-chemical model (UNIQUAC). UNIQUAC equations [20] are given by:

$$\ln\gamma_i = \ln\gamma_i^C + \ln\gamma_i^R \tag{1}$$

$$\ln\gamma_i^C = \ln\frac{\phi_i}{x_i} + \frac{Z}{2}\ln\frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i}\sum_{j=1}^{n} x_j l_j \tag{2}$$

$$\ln\gamma_i^R = q_i\left(1 - \ln\sum_{j=1}^{n}\theta_j\tau_{ji} - \sum_{j=1}^{n}\frac{\theta_i\tau_{ij}}{\sum_{k=1}^{n}\theta_k\tau_{kj}}\right) \tag{3}$$

$$\phi_i = \frac{x_i r_i}{\sum_{i=1}^{n} x_i r_i}\ ;\ \theta_i = \frac{x_i q_i}{\sum_{i=1}^{n} x_i q_i} \tag{4}$$

$$\tau_{ij} = \tau_{ij}^0 + \tau_{ij}^T(T - T_{ref})\ ;\ \tau_{ji} = \tau_{ji}^0 + \tau_{ji}^T(T - T_{ref}) \tag{5}$$

Table 1: Chemical reaction equilibrium constants: $ln\,K = a_1 + a_2/T$.

Reaction	Phase	Heat of reaction (kJ/mol)	a_1	a_2	References
$W + FA \Leftrightarrow MG$	Vapor	-43.51	-16.984	5233.2	[19]
$2MG \Leftrightarrow MG_2 + W$	Liquid	-0.234	$4.98.10^{-3}$	869.5	[17, 18]
$MG + MG_2 \Leftrightarrow MG_3 + W$ $MG + MG_3 \Leftrightarrow MG_4 + W$ $MG + MG_4 \Leftrightarrow MG_5 + W$ $MG + MG_5 \Leftrightarrow MG_6 + W$ $MG + MG_6 \Leftrightarrow MG_7 + W$	Liquid	-0.234	$1.908.10^{-2}$	544.5	[17, 18]
$ME + FA \Leftrightarrow HF$	Vapor	-53.73	-14.755	5969.4	[14]
$2HF \Leftrightarrow HF_2 + ME$ $HF + HF_2 \Leftrightarrow HF_3 + ME$ $HF + HF_3 \Leftrightarrow HF_4 + ME$ $HF + HF_4 \Leftrightarrow HF_5 + ME$ $HF + HF_5 \Leftrightarrow HF_6 + ME$ $HF + HF_6 \Leftrightarrow HF_7 + ME$	Liquid	-7.00	-0.4966	-491.3	[14]

UNIQUAC is an empirical model that requires experimental data to identify binary interaction parameters. Therefore, it is not totally predictive as the UNIFAC model. This model has proved to give a good description of polar mixtures. Also, it makes it possible to handle complex multicomponent mixtures, as it is the case here, from the knowledge of identified binary interaction parameters of all involved binary sub-systems. In the case of the formaldehyde-water-methanol system, the model is likely to describe the behavior of both small molecules (FA, W, ME, HF, MG) and larger ones (MG_2 - MG_7, HF_2 - HF_7). Indeed, as we already mentioned, the UNIQUAC model was also chosen for its ability to account for the influence of the size and the form of the molecules in a mixture thanks to the combinatorial term of equation 1. The residual term of equation 1 characterizes energetic interactions between molecules and requires the identification of the binary interaction parameters. The temperature dependency of the binary interaction parameters τ_{ij} and τ_{ji} is also accounted by equation 5. The identification of the binary interaction parameters is developed in the section 3. The oligomer distribution in the liquid phase is obtained from mass balances, assuming chemical equilibrium. Overall compositions are calculated from mass balances. They are given by equations 6 to 9.

$$x_{FA}^{overall} = s.(x_{FA} + x_{MG} + \sum\nolimits_{i=2}^{7} i.x_{MG_i} + x_{HF} + \sum\nolimits_{i=2}^{7} i.x_{HF_i}) \tag{6}$$

$$x_{W}^{overall} = s.(x_{W} + x_{MG} + \sum\nolimits_{i=2}^{7} x_{MG_i}) \tag{7}$$

$$x_{ME}^{overall} = s.(x_{ME} + x_{HF} + \sum\nolimits_{i=2}^{7} x_{HF_i}) \tag{8}$$

$$s = (1 + x_{MG} + \sum\nolimits_{i=2}^{7} i.x_{MG_i} + x_{HF} + \sum\nolimits_{i=2}^{7} i.x_{HF_i})^{-1} \tag{9}$$

These fractions are calculated for every Pxy diagram.

2.3. Description of the vapor phase

From a physical point of view and as the model is to be used in low pressure conditions, the vapor phase is assumed to behave as a mixture of ideal gases. It contains water, methanol, formaldehyde, methylene glycol and hemiformal. The chemical reaction equilibria for the formation of methylene glycol and hemiformal were accounted for through the chemical-reaction equilibrium constants described in the next section.

2.4. Equations of the reactive vapor-liquid equilibrium model

The uncoupled approach adopted to model the reactive vapor-liquid equilibrium leads to equations 10 to 15. The equations for the saturation vapor pressures (see equation 11) of the components were taken from literature [18] and their coefficients are given in table 2.

$$y_i P = x_i \gamma_i (T, x) P_i^S (T) \tag{10}$$

$$\ln P_i^S (T)/kPa = A + \frac{B}{T/K + C} \tag{11}$$

$$K_{MG} = \frac{y_{MG}}{y_{FA} y_W} . \frac{P_{ref}}{P} \tag{12}$$

$$K_{MG_n} = \frac{x_{MG_n} x_W}{x_{MG} x_{MG_{n-1}}} . \frac{\gamma_{MG_n} \gamma_W}{\gamma_{MG} \gamma_{MG_{n-1}}} \tag{13}$$

$$K_{HF} = \frac{y_{HF}}{y_{FA} y_{ME}} . \frac{P_{ref}}{P} \tag{14}$$

$$K_{HF_n} = \frac{x_{HF_n} x_{ME}}{x_{HF} x_{HF_{n-1}}} . \frac{\gamma_{HF_n} \gamma_{ME}}{\gamma_{HF} \gamma_{HF_{n-1}}} \tag{15}$$

As explained above, the activity coefficients are calculated in this work with the UNIQUAC model (see equations 1 to 5).

Note that when the vapor-liquid equilibrium equations and the chemical reaction equilibrium equations in one phase are satisfied, the chemical-reaction equilibrium equations in the other phase are automatically satisfied.

Table 2: Antoine coefficients for pure component vapor pressures $ln\ P^S = A + B/(T + C)$ [18]

Component	***A***	***B***	***C***
Formaldehyde	14.4625	-2 204.13	-30.0
Water	16.2886	-3 816.44	-46.13
Methanol	16.5725	-3 626.55	-34.29
Methylene Glycol	19.5527	-6 189.19	-9.15
Hemiformal	19.5736	-5 646.71	0.00

3. Determination of the UNIQUAC binary interaction parameters

The not reactive water-methanol binary has been widely studied in the literature. Nevertheless, as the reported binary interaction parameters may have been estimated with other values of the pure component properties than those used in this study, they were identified again in this work using experimental data recommended by the DECHEMA in the pressure and temperature range of [267 mbar-1013 mbar] and [35°C-100°C] respectively [21, 22].

Other binaries involve chemical reactions. To avoid spreading the uncertainty of the value of the chemical equilibrium constant into the physical equilibrium parameters, the binary interaction parameter estimation has been performed on non-reactive VLE data. In consequence, only vapor-liquid equilibrium equations are needed to estimate the binary interaction coefficients (equations 1 to 5 and 10 to 11). As it is impossible to uncouple chemical and physical equilibria for these systems in practice, no experimental data are available for the non-reactive vapor-liquid equilibrium. So simulated vapor-liquid data were generated using the UNIFAC Original model.

The objective function is usually defined as the residual between experimental data and estimated vapor-liquid flash calculations. Indeed, it was not possible to use experimental data in our case because of the presence of the chemical reactions. Therefore, vapor-liquid data were generated using the UNIFAC Original model as developed by the group of Maurer [18]. In consequence, the objective function was defined as the residual between UNIQUAC and UNIFAC Original estimated pressures and mole fractions:

$$F_{obj} = \frac{F_{obj,bubble} + F_{obj,dew}}{n_{bubble} + n_{dew}} \tag{16}$$

with

$$F_{obj,bubble} = \sum_{i=1}^{n_{bubble}} \frac{(|y_{1,UNIFAC}^{bubble} - y_{1,calc}^{bubble}|)_i}{\bar{y}_{i,1}^{bubble}} + \frac{(|y_{2,UNIFAC}^{bubble} - y_{2,calc}^{bubble}|)_i}{\bar{y}_{i,2}^{bubble}} + \frac{(|P_{UNIFAC}^{bubble} - P_{calc}^{bubble}|)_i}{\bar{P}_i^{\ bubble}} \tag{17}$$

$$\forall\, i \,\epsilon\, [1; n_{bulle}]\; \bar{y}_{i,1}^{bubble} = \frac{(y_{1,UNIFAC}^{bubble} + y_{1,calc}^{bubble})_i}{2};\; \bar{y}_{i,2}^{bubble} = \frac{(y_{i,2,UNIFAC}^{bubble} + y_{i,2,calc}^{bubble})_i}{2};\; \bar{P}_i^{bubble} = \frac{(P_{i,UNIFAC}^{bubble} + P_{i,calc}^{bubble})_i}{2} \tag{18}$$

and

$$F_{obj,dew} = \sum_{i=1}^{n_{dew}} \frac{(|y_{1,UNIFAC}^{dew} - y_{1,calc}^{dew}|)_i}{\bar{y}_{i,1}^{dew}} + \frac{(|y_{2,UNIFAC}^{dew} - y_{2,calc}^{dew}|)_i}{\bar{y}_{i,2}^{dew}} + \frac{(|P_{UNIFAC}^{dew} - P_{calc}^{dew}|)_i}{\bar{P}_i^{dew}} \tag{19}$$

$$\forall\, i \,\epsilon\, [1; n_{dew}]\; \bar{y}_{i,1}^{dew} = \frac{(y_{1,UNIFAC}^{dew} + y_{1,calc}^{dew})_i}{2};\; \bar{y}_{i,2}^{dew} = \frac{(y_{2,UNIFAC}^{dew} + y_{2,calc}^{dew})_i}{2};\; \bar{P}_i^{dew} = \frac{(P_{UNIFAC}^{dew} + P_{calc}^{dew})_i}{2} \tag{20}$$

UNIQUAC binary interaction parameters have to be identified for systems including water, methanol, formaldehyde, methylene glycol, hemiformal, poly(oxymethylene) glycols (MG_2 - MG_7), and poly(oxymethylene) hemiformals (HF_2 - HF_7). Without any assumption, binary interaction parameters of 136 binaries should have been identified. Some preliminary calculations, validated by using UNIFAC Original, showed that it was not worth differentiating the binary interaction parameters of the polymers of the methylene glycol and poly(oxymethylene) glycol with other components except for formaldehyde. This consists in neglecting the size effect in the second term of the residual part of the activity coefficient for these compounds. Finally, 33 set of parameters were identified by solving the following optimization problem:

$$\min_{\tau_{ij}^0, \tau_{ij}^T, \tau_{ji}^0, \tau_{ji}^T} F_{obj} \tag{21}$$

The identification was done using the Matlab function fminsearch which is a multidimensional unconstrained nonlinear method of minimization (Nelder-Mead) and which was coupled with the Simulis Thermodynamics Toolbox in our case.

4. Results and Discussions

4.1. UNIQUAC binary interaction parameters

The UNIQUAC binary interaction parameters were obtained by minimizing the objective function defined by equation 16. For all data points in this work, the relative mean error was calculated. The value of the objective function indicated a good estimation of the UNIQUAC binary interaction parameters. UNIQUAC binary interaction parameters that were determined in this work are given in tables 3 to 6.

Table 3 reports the water-methanol UNIQUAC estimated binary interaction parameters.

Table 3: Water - Methanol UNIQUAC estimated binary interaction parameters

Component 1	***Component 2***	τ_{ij}^0	τ_{ij}^T	τ_{ji}^0	τ_{ji}^T	***References***
Methanol (ME)	Water (W)	156	-369	0.91	0.20	[21, 22]

Table 4 shows the UNIQUAC binary interaction parameters of the formaldehyde-water system and table 5 reports the UNIQUAC binary interaction parameters of the formaldehyde-methanol system. The table 6 shows the binary interaction parameters to add to deal with the water-formaldehyde-methanol ternary system.

4.2. Comparison with literature data

To check the validity of this approach, the reactive vapor-liquid model was solved. The activity coefficients were calculated by using either the UNIQUAC model with binary interaction parameters identified in this work (chemUNIQUAC model) or the UNIFAC Original model (chemUNIFAC model). The results were compared to experimental data taken from the literature for the formaldehyde-water system [17], formaldehyde-methanol system [23], and formaldehyde-water-methanol system [18].

Table 4: Formaldehyde-Water system UNIQUAC estimated binary interaction parameters

Component 1	***Component 2***	τ^0_{ij}	τ^T_{ij}	τ^0_{ji}	τ^T_{ji}
Formaldehyde (FA)	Water (W)	967	-169	1.94	-0.23
Formaldehyde (FA)	Methylene Glycol (MG)	2714	190	2.21	-2.74
Formaldehyde (FA)	Methylene Glycol 2 (MG_2)	-274	506	-0.05	-1.72
Formaldehyde (FA)	Methylene Glycol 3 (MG_3)	-22	153	-0.28	-1.75
Formaldehyde (FA)	Methylene Glycol 4 (MG_4)	-54	149	0.12	-2.36
Formaldehyde (FA)	Methylene Glycol 5 (MG_5)	26	75	0.09	-2.59
Formaldehyde (FA)	Methylene Glycol 6 (MG_6)	32	32	0.24	-2.82
Formaldehyde (FA)	Methylene Glycol 7 (MG_7)	35	31	0.32	-3.08
Water (W)	Methylene Glycol (MG)	431	-399	0.16	-0.25
Water (W)	Poly(oxymethylene) glycols ($MG_{i\geq2}$)	65	-299	0.18	0.76
Methylene Glycol (MG)	Poly(oxymethylene) glycols ($MG_{i\geq2}$)	977	-945	-1.56	2.18
Poly(oxymethylene) glycols ($MG_{i\geq2}$)	Poly(oxymethylene) glycols ($MG_{j\geq2,j\neq i}$)	140	-103	-0.0067	-0.034

Table 5: Formaldehyde-Methanol system UNIQUAC estimated binary interaction parameters

Component 1	***Component 2***	τ^0_{ij}	τ^T_{ij}	τ^0_{ji}	τ^T_{ji}
Formaldehyde (FA)	Methanol (ME)	577	-251	0.29	-0.4
Formaldehyde (FA)	Hemiformal (HF)	-54	76	-0.46	-0.72
Formaldehyde (FA)	Hemiformal 2 (HF_2)	-37	58	-0.28	-1.36
Formaldehyde (FA)	Hemiformal 3 (HF_3)	-25	31	-0.02	-1.87
Formaldehyde (FA)	Hemiformal 4 (HF_4)	-3	11	0.14	-2.26
Formaldehyde (FA)	Hemiformal 5 (HF_5)	-18	18	0.32	-2.61
Formaldehyde (FA)	Hemiformal 6 (HF_6)	-19	17	0.42	-2.88
Formaldehyde (FA)	Hemiformal 7 (HF_7)	-19	16	0.55	-3.16
Methanol (ME)	Hemiformal (HF)	26	-38	-0.85	0.13
Methanol (ME)	Poly(oxymethylene) hemiformal ($HF_{i\geq2}$)	12	0.24	-0.10	-1.36
Hemiformal (HF)	Poly(oxymethylene) hemiformal ($HF_{i\geq2}$)	-24	23	1.47	-1.47
Poly(oxymethylene) hemiformal ($HF_{i\geq2}$)	Poly(oxymethylene) hemiformal ($HF_{j\geq2,j\neq i}$)	37	-26	0.43	-0.47

Table 6: Formaldehyde-Water-Methanol system UNIQUAC estimated binary interaction parameters

Component 1	***Component 2***	τ^0_{ij}	τ^T_{ij}	τ^0_{ji}	τ^T_{ji}
Hemiformal (HF)	Water (W)	825	-16	-2.97	2.17
Hemiformal (HF)	Methylene Glycol (MG)	-291	-16	1.35	0.63
Hemiformal (HF)	Poly(oxymethylene) glycols ($MG_{i\geq2}$)	501	-97	2.58	-1.09
Poly(oxymethylene) hemiformal ($HF_{i\geq2}$)	Water (W)	457	985	-2.00	0.41
Poly(oxymethylene) hemiformal ($HF_{i\geq2}$)	Methylene Glycol (MG)	-21	663	0.46	1.00
Poly(oxymethylene) hemiformal ($HF_{i\geq2}$)	Poly(oxymethylene) glycols ($MG_{j\geq2,j\neq i}$)	878	-94	0.00	0.00
Methanol (ME)	Methylene Glycol (MG)	15	-130	-0.39	0.03
Methanol (ME)	Poly(oxymethylene) glycols ($MG_{i\geq2}$)	206	-333	-0.84	-0.55

For all systems, the average overall deviation in the gas-phase composition and the average overall deviation of the pressure between experimental data and our work were calculated as:

$$\overline{\Delta\tilde{y}^{model}_{FA}} = \frac{1}{n_{exp}}\sum_{l=1}^{n_{exp}}\frac{(|\tilde{y}_{FA,exp}-\tilde{y}_{FA,model}|)_l}{\bar{y}_{FA,l}} \tag{22}$$

$$\overline{\Delta\tilde{y}^{model}_{ME}} = \frac{1}{n_{exp}}\sum_{l=1}^{n_{exp}}\frac{(|\tilde{y}_{ME,exp}-\tilde{y}_{ME,model}|)_l}{\bar{y}_{ME,l}} \tag{23}$$

$$\overline{\Delta P^{model}} = \frac{1}{n_{exp}}\sum_{l=1}^{n_{exp}}\frac{(|P_{exp}-P_{model}|)_l}{\bar{P}_l} \tag{24}$$

with $model = chemUNIQUAC$ or $chemUNIFAC$ and $\forall\, l \in [1; n_{exp}]\bar{y}_{FA,l} = \frac{(\tilde{y}_{FA,exp}+\tilde{y}_{FA,model})_l}{2}$; $\bar{y}_{ME,l} = \frac{(\tilde{y}_{ME,exp}+\tilde{y}_{ME,model})_l}{2}$; $\bar{P}_l = \frac{(P_{exp}+P_{model})_l}{2}$.

Concerning the accuracy of the experimental data from the literature, formaldehyde concentrations were determined with a relative error of less than 2%. The temperature and the pressure were measured with an accuracy of ± 0.1K and ± 0.5 kPa respectively [17].

4.2.1. Water-Methanol System

The average deviation of the gas-phase composition and average deviation of the temperature were calculated for the water-methanol binary and are reported in table 7.

Table 7: Average deviation of the gas-phase composition and average deviation of the temperature for water-methanol binary using UNIQUAC.

Compound 1	Compound 2	Type of diagram	$\overline{\Delta T}$ (%)	$\overline{\Delta y_1}$ (%)	References
Water	Methanol	P = 1013 mbar	0.18	1.90	[21]
Water	Methanol	P = 666 mbar	0.43	3.58	[22]
Water	Methanol	P = 466 mbar	0.84	5.46	[22]
Water	Methanol	P = 266 mbar	0.57	6.37	[22]

4.2.2. Formaldehyde-Water System

Table 8 compares the average overall deviation of the gas-phase composition and average deviation of the pressure for the water-formaldehyde system between experimental data from the literature [17] and the two models (chemUNIQUAC and chemUNIFAC). Furthermore, the average deviation of the polymer distribution in liquid-phase, between experimental data [17] and the two models (chemUNIQUAC and chemUNIFAC), were calculated using equation 25 (see tables 9 and 10).

$$\overline{\Delta x^{model}_{MG_n}} = \frac{1}{n_{exp}}\sum_{l=1}^{n_{exp}}\frac{(|x_{MG_n,exp}-x_{MG_n,model}|)_l}{\bar{x}_{MG_n,l}} \tag{25}$$

with n the degree of polymerization and $model = chemUNIQUAC$ or $chemUNIFAC$ and $\forall\, l \in [1; n_{exp}]$ $\bar{x}_{MG_n,l} = \frac{(x_{MG_n,exp}+x_{MG_n,model})_l}{2}$.

The values of the deviations indicate that the chemUNIQUAC model provides a fairly good description of the formaldehyde-water system. Figure 3 shows the isothermal phase diagram at 383K. Good results were obtained for the prediction of the overall composition (a) and the distribution of the polymers in the liquid phase (b). Our model (solid line) was compared with the original chemUNIFAC model (dashed line). Our model is shown to be able to predict the overall composition and the distribution of polymers at high concentrations of formaldehyde. At 383K, the pressure prediction (c) was not as accurate as composition. Nonetheless, the figure 5 shows that the higher the equilibrium temperature, the more accurate the calculation of the pressure. Also, chemUNIQUAC model gives a better description of the azoetropic point.

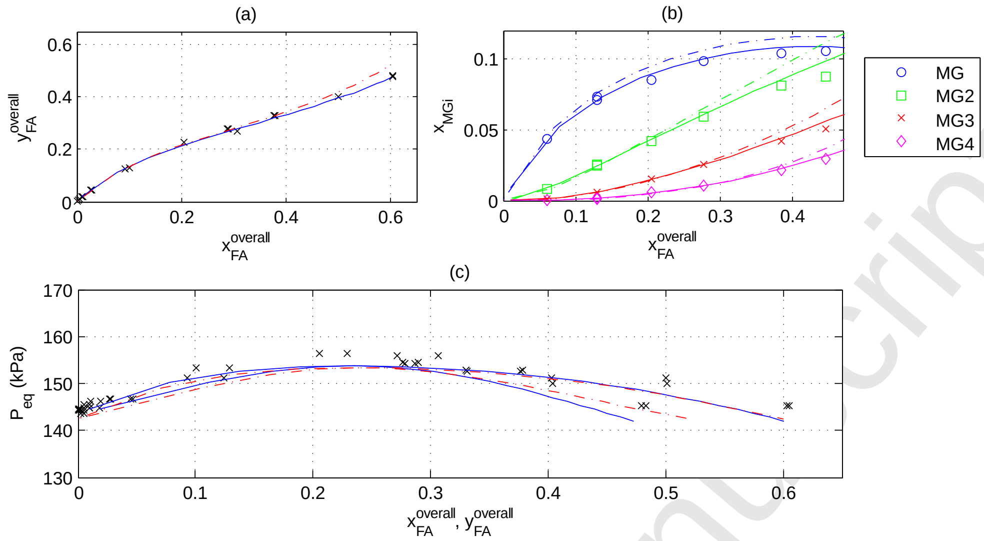

Figure 3: Prediction of formaldehyde-water system vapor-liquid and chemical equilibria at 383K: (a) overall composition of formaldehyde in vapor phase vs overall composition of formaldehyde in liquid phase, (b) concentration of methylene glycol (MG) and polyoxymethylene glycols (MG_2, MG_3, MG_4) in chemical equilibria and (c) Pxy isothermal phase diagram. (×) experimental values from the literature [17]. Solid line: predicted phase diagram with chemUNIQUAC. Dashed line: predicted phase diagram with chemUNIFAC.

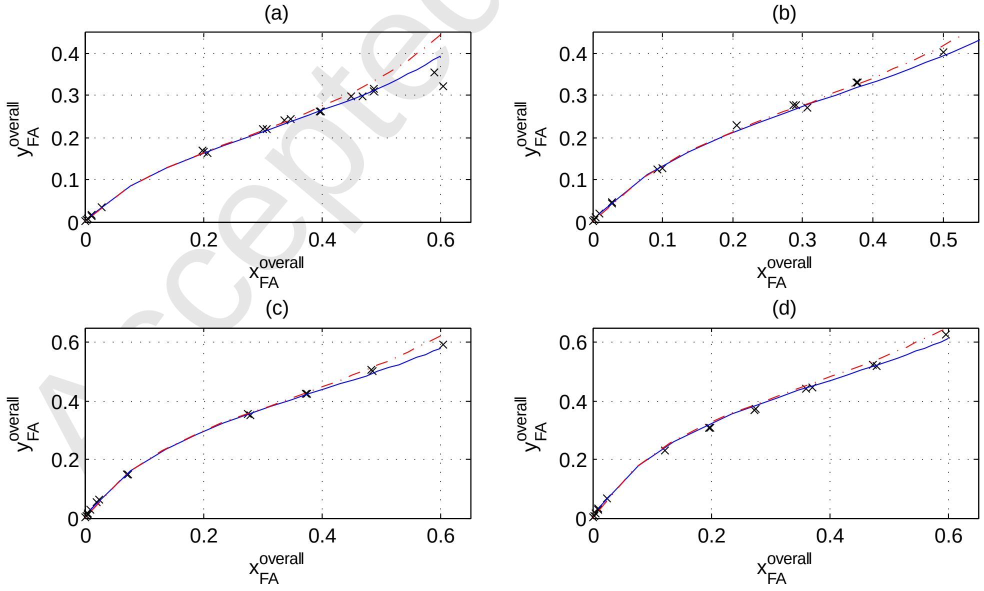

Figure 4: Prediction of isothermal phase diagrams for water-formaldehyde system at four different temperatures (a) 363K (b) 383K (c) 413K and (d) 423K. (×) experimental values from the literature [17]. Solid line: predicted phase diagram with chemUNIQUAC. Dashed line: predicted phase diagram with chemUNIFAC.

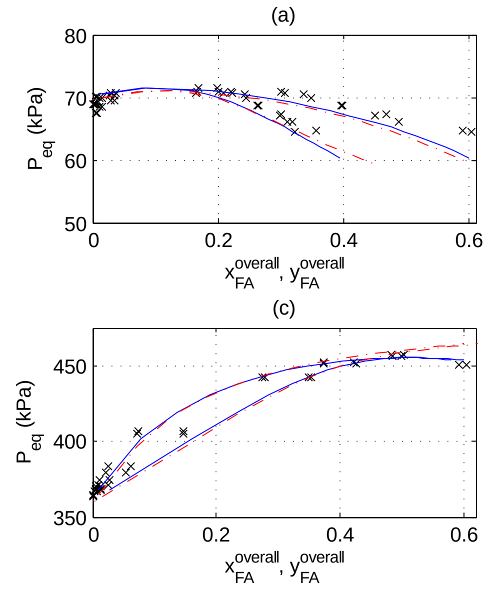

Figure 5: Prediction of Pxy isothermal phase diagrams for water-formaldehyde system at four different temperatures (a) 363K (b) 383K (c) 413K and (d) 423K. (×) experimental values from the literature [17]. Solid line: predicted phase diagram with chemUNIQUAC. Dashed line: predicted phase diagram with chemUNIFAC.

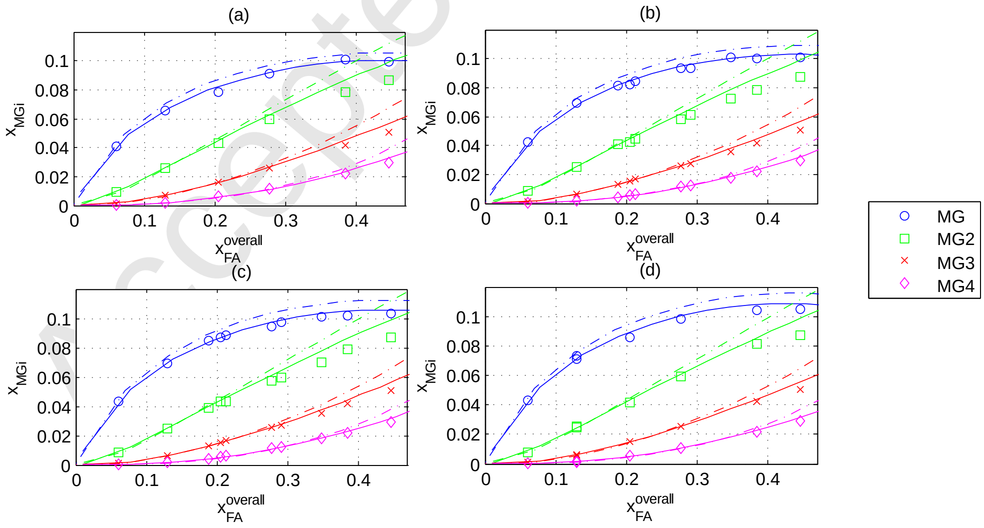

Figure 6: Distribution of methylene glycol (MG) and polyoxymethylene glycols (MG_2, MG_3, MG_4) in chemical equilibria at different temperatures: (a) 338K, (b)353K, (c) 368K and (d) 383K. (×) experimental values from the literature [17]. Solid line: predicted phase diagram with chemUNIQUAC. Dashed line: predicted phase diagram with chemUNIFAC.

Table 8: Average overall deviation of the gas-phase composition and average overall deviation of the pressure for the water-formaldehyde system using chemUNIQUAC model and chemUNIFAC model.

	$\overline{\Delta\tilde{y}_{FA}}(\%)$		$\overline{\Delta P}(\%)$	
Temperature (K)	chemUNIQUAC	chemUNIFAC	chemUNIQUAC	chemUNIFAC
363	4.41	4.93	2.19	2.20
383	2.89	3.72	1.51	1.46
413	0.86	1.70	0.60	0.96
423	1.75	3.89	0.36	1.53

Table 9: Average deviation in liquid-phase of the polymer distribution for the water-formaldehyde system using chemUNIQUAC model and chemUNIFAC model (1/2)

	$\overline{\Delta x_{MG}}$		$\overline{\Delta x_{MG_2}}$	
Temperature (K)	chemUNIQUAC	chemUNIFAC	chemUNIQUAC	chemUNIFAC
338	1.59	6.97	5.89	13.3
353	1.82	6.85	5.64	12.7
368	1.28	7.11	6.09	13.6
383	3.05	8.33	5.60	11.9

Table 10: Average deviation in liquid-phase of the polymer distribution for the water-formaldehyde system using chemUNIQUAC model and chemUNIFAC model (2/2)

	$\overline{\Delta x_{MG_3}}$		$\overline{\Delta x_{MG_4}}$	
Temperature (K)	chemUNIQUAC	chemUNIFAC	chemUNIQUAC	chemUNIFAC
338	5.08	15.2	5.25	18.1
353	4.62	13.5	6.05	17.7
368	6.43	11.5	11.5	14.5
383	10.7	18.0	19.0	26.8

Figures 4 and 5 show results for formaldehyde-water system at four temperatures: (a) 363K, (b) 383K, (c) 413K, (d) 423K. Figure 4 presents the overall composition of formaldehyde in vapor phase vs overall composition of formaldehyde in liquid phase. Good agreement was obtained between experimental data and the prediction of the overall composition with the chemUNIQUAC model. Figure 4 confirms that the chemUNIQUAC model provides a better description of the composition at high concentration of formaldehyde. The figure 5 shows the Pxy isothermal phase diagram where the higher the temperature, the better the prediction of pressure.

Figure 6 shows the distribution of methylene glycol (MG) and polyoxymethylene glycols (MG_2, MG_3, MG_4) at four temperatures: (a) 338K (b) 353K (c) 368K and (d) 383K. This figure points out the interest of the chemUNIQUAC model which gives good prediction of the polymers distribution in the liquid phase.

4.2.3. Formaldehyde-Methanol System

Table 11 compares the average overall deviation of the gas-phase composition and average deviation of the pressure for the methanol-formaldehyde system between experimental data from the literature [23] and the two models (chemUNIQUAC and chemUNIFAC).

The values of the deviations reported in table 11 indicate that the proposed chemUNIQUAC model provides a good representation of the formaldehyde-methanol system, equivalent to the chemUNIFAC. Figures 7 to 9 show the prediction of formaldehyde-methanol system vapor-liquid and chemical equilibria at three temperatures (333K, 343K, and 353K). The part (a) of each figure illustrates the overall composition of formaldehyde in vapor phase vs overall composition of formaldehyde in liquid phase and the part (b) the Pxy isothermal phase diagram. Good agreement with experimental data was obtained with both models. Experimental distributions of the polyoxymethylene hemiformals

Table 11: Average overall deviation in gas-phase of the composition and average overall deviation of the pressure for the methanol-formaldehyde system using chemUNIQUAC model and chemUNIFAC model.

	$\overline{\Delta\tilde{y}_{FA}}(\%)$		$\overline{\Delta P}(\%)$	
Temperature (K)	chemUNIQUAC	chemUNIFAC	chemUNIQUAC	chemUNIFAC
333	9.08	6.33	2.65	1.89
343	5.04	4.67	2.57	3.72
353	5.26	5.16	3.21	4.21

could not be plotted because not available in the literature. Indeed, formaldehyde is rarely stored with pure methanol; aqueous solutions of formaldehyde with or without methanol are the usual way to handle it.

4.2.4. *Formaldehyde-Water-Methanol System*

Table 12 compares the average overall deviation of the gas-phase composition and average deviation of the pressure for the formaldehyde-water-methanol system between experimental data from the literature [18] and the two models (chemUNIQUAC and chemUNIFAC), calculated with equations 22 to 24.

The values of the deviations show that the chemUNIQUAC model provides more accurate description of the formaldehyde-water-methanol system than the chemUNIFAC model.

Table 12: Average overall deviation in gas-phase of the composition and average overall deviation of the pressure for themethanol-formaldehyde system using chemUNIQUAC model and chemUNIFAC model.

	$\overline{\Delta\tilde{y}_{ME}}(\%)$		$\overline{\Delta\tilde{y}_{FA}}(\%)$		$\overline{\Delta P}(\%)$	
Temperature (K)	chemUNIQUAC	chemUNIFAC	chemUNIQUAC	chemUNIFAC	chemUNIQUAC	chemUNIFAC
333	0.66	0.70	0.93	4.07	0.25	0.26

Table 13 reports a comparison between experimental data in the literature [18], predicted equilibria with chemUNIQUAC and with chemUNIFAC. Overall deviation in the gas-phase and deviation of the pressure between experimental data and models were calculated for each equilibrium data.

In this case also, the values of the deviations for each composition confirm that the chemUNIQUAC model provides a better representation of the formaldehyde-water-methanol system than the chemUNIFAC model.

5. Conclusions and Perspectives

The improved approach using UNIQUAC coupled with chemical reactions (so-called here as the chemUNIQUAC model) was proved to quantitatively describes the reactive vapor-liquid equilibrium of formaldehyde-water system, formaldehyde-methanol system and formaldehyde-water-methanol system. The chemUNIQUAC model was shown to provide a better description of the composition at high concentration of formaldehyde than the original UNIFAC model. This model provides a reliable description of the vapor-liquid and chemical equilibria from about 330K to 420K, for dilute as well as for concentrated solutions. It also accurately describes the oligomer distribution in the liquid-phase. The main interest of our model lies in its good ability to predict the overall composition and the distribution of polymers at high concentrations of formaldehyde.

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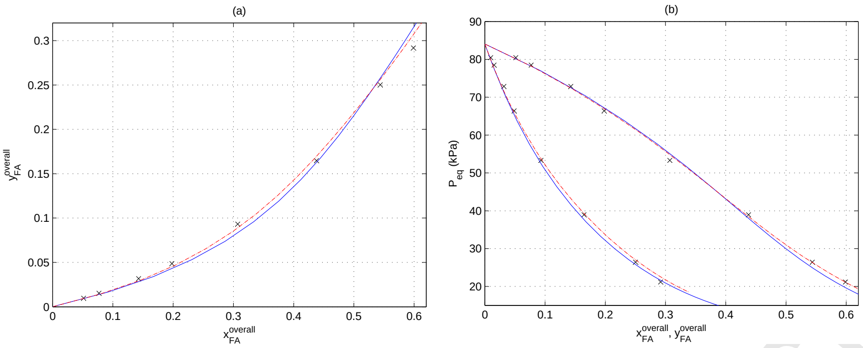

Figure 7: Prediction of formaldehyde-methanol system vapor-liquid and chemical equilibria at 333K: (a) overall composition of formaldehyde in vapor phase vs overall composition of formaldehyde in liquid phase, (b) Pxy isothermal phase diagram. (×) experimental values from the literature [23]. Solid line: predicted phase diagram with chemUNIQUAC. Dashed line: predicted phase diagram with chemUNIFAC.

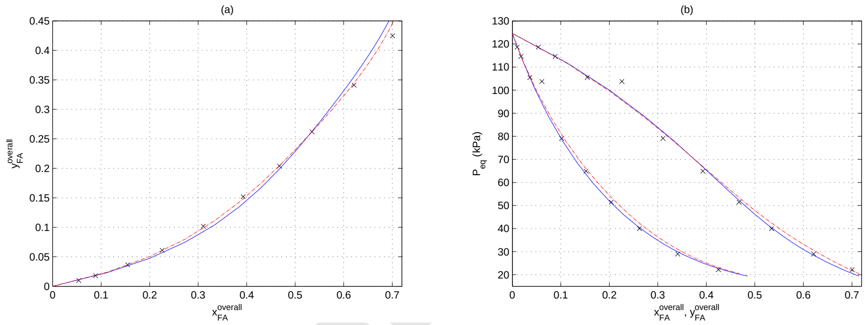

Figure 8: Prediction of formaldehyde-methanol system vapor-liquid and chemical equilibria at 343K: (a) overall composition of formaldehyde in vapor phase vs overall composition of formaldehyde in liquid phase, (b) Pxy isothermal phase diagram. (×) experimental values from the literature [23]. Solid line: predicted phase diagram with chemUNIQUAC. Dashed line: predicted phase diagram with chemUNIFAC.

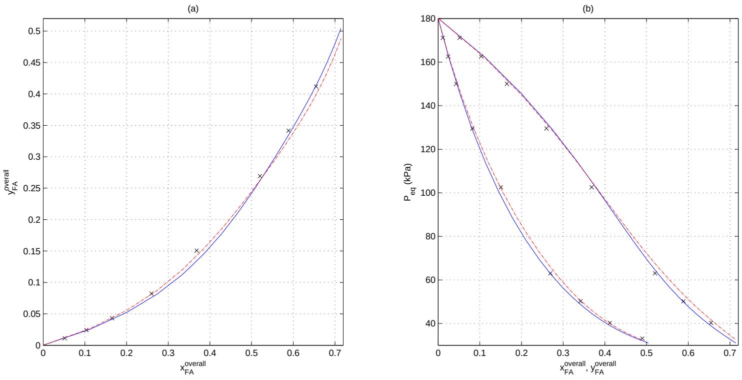

Figure 9: Prediction of formaldehyde-methanol system vapor-liquid and chemical equilibria at 353K: (a) overall composition of formaldehyde in vapor phase vs overall composition of formaldehyde in liquid phase, (b) Pxy isothermal phase diagram. (×) experimental values from the literature [23]. Solid line: predicted phase diagram with chemUNIQUAC. Dashed line: predicted phase diagram with chemUNIFAC.

Table 13: Prediction of formaldehyde-water-methanol system vapor-liquid and chemical equilibria at 333K. Exp: Experimental values from the literature [18]. Calc1: predicted phase equilibria with chemUNIQUAC. Calc2: predicted phase equilibria with chemUNIFAC.

			Pressure (kPa)			$\overline{\Delta P}(\%)$			$\tilde{y}_{FA}(\%)$		$\overline{\Delta \tilde{y}_{FA}}(\%)$			$\tilde{y}_{ME}(\%)$		$\overline{\Delta \tilde{y}_{ME}}(\%)$	
T (K)	$\tilde{x}_{FA}(\%)$	$\tilde{x}_{ME}(\%)$	***Exp***	***Calc1***	***Calc2***	***Calc1***	***Calc2***	***Exp***	***Calc1***	***Calc2***	***Calc1***	***Calc2***	***Exp***	***Calc1***	***Calc2***	***Calc1***	***Calc2***
333	0.0057	0.0084	20.5	20.9	21.16	0.06	0.11	0.0052	0.0049	0.0084	0.17	1.73	0.0583	0.0615	0.0738	0.18	0.78
333	0.0059	0.0061	20.2	20.6	20.79	0.06	0.10	0.0051	0.0052	0.0061	0.05	0.55	0.0453	0.0455	0.0549	0.01	0.64
333	0.0058	0.0173	21.7	22.0	22.57	0.05	0.13	0.0056	0.0048	0.0173	0.51	3.77	0.1155	0.1183	0.1391	0.08	0.62
333	0.0059	0.0145	21.2	21.7	22.14	0.08	0.14	0.0055	0.0050	0.0145	0.35	3.27	0.0974	0.1012	0.1197	0.13	0.69
333	0.0061	0.0286	23.3	23.5	24.26	0.02	0.13	0.0061	0.0048	0.0286	0.80	4.75	0.1823	0.1805	0.2077	0.03	0.43
333	0.0060	0.0297	23.5	23.6	24.42	0.01	0.13	0.0059	0.0047	0.0297	0.76	4.84	0.1816	0.1860	0.2137	0.08	0.54
333	0.0062	0.0547	26.5	26.5	27.80	0.00	0.16	0.0056	0.0044	0.0547	0.79	5.67	0.2915	0.2934	0.3253	0.02	0.37
333	0.0068	0.0131	34.8	21.5	36.04	1.57	0.12	0.0043	0.0057	0.1312	0.95	6.11	0.5055	0.0925	0.5140	4.60	0.06
333	0.0074	0.2029	41.1	40.2	41.95	0.07	0.07	0.0033	0.0040	0.2029	0.63	6.41	0.6059	0.5957	0.6078	0.06	0.01
333	0.0082	0.4130	53.5	53.8	54.84	0.02	0.08	0.0021	0.0041	0.4130	2.16	6.54	0.7765	0.7592	0.7569	0.08	0.09
333	0.0082	0.4144	53.5	53.9	54.91	0.02	0.09	0.0021	0.0041	0.4144	2.16	6.54	0.7573	0.7600	0.7576	0.01	0.00
333	0.0089	0.6398	63.4	65.8	66.35	0.12	0.15	0.0016	0.0049	0.6398	3.36	6.57	0.8501	0.8634	0.8599	0.05	0.04
333	0.0317	0.0111	20.2	21.2	21.43	0.16	0.20	0.0246	0.0239	0.0111	0.10	2.44	0.0549	0.0795	0.0918	1.22	1.68
333	0.0312	0.0138	20.5	21.5	21.84	0.16	0.21	0.0250	0.0232	0.0138	0.24	1.70	0.0648	0.0968	0.1113	1.32	1.76
333	0.0312	0.0297	22.1	23.5	24.16	0.21	0.30	0.0261	0.0216	0.0297	0.63	1.05	0.1371	0.1861	0.2085	1.01	1.38
333	0.0312	0.0319	22.2	23.8	24.46	0.23	0.32	0.0264	0.0214	0.0319	0.70	1.32	0.1482	0.1969	0.2200	0.94	1.30
333	0.0317	0.0601	25.0	27.0	28.10	0.26	0.39	0.0246	0.0195	0.0601	0.77	3.40	0.2612	0.3129	0.3386	0.60	0.86
333	0.0323	0.0581	25.0	26.8	27.85	0.23	0.36	0.0257	0.0200	0.0581	0.84	3.26	0.2531	0.3059	0.3314	0.63	0.89
333	0.0341	0.1373	32.9	34.7	36.09	0.18	0.31	0.0211	0.0172	0.1373	0.68	5.18	0.4561	0.5030	0.5196	0.33	0.43
333	0.0355	0.2077	39.5	40.5	41.83	0.09	0.19	0.0175	0.0161	0.2077	0.28	5.71	0.5698	0.6023	0.6110	0.18	0.23
333	0.0348	0.2092	39.5	40.7	41.95	0.10	0.20	0.0171	0.0158	0.2092	0.27	5.73	0.5676	0.6039	0.6126	0.21	0.25
333	0.0369	0.3880	49.8	52.5	53.42	0.18	0.23	0.0122	0.0147	0.3880	0.63	6.18	0.7224	0.7464	0.7475	0.11	0.11
333	0.0377	0.3792	49.4	52.0	52.91	0.17	0.23	0.0121	0.0150	0.3792	0.72	6.16	0.7291	0.7413	0.7425	0.06	0.06
333	0.0433	0.6155	61.5	65.0	65.81	0.18	0.23	0.0099	0.0166	0.6155	1.69	6.32	0.8662	0.8558	0.8598	0.04	0.02
333	0.0436	0.6343	61.5	66.0	66.79	0.24	0.28	0.0098	0.0168	0.6343	1.76	6.32	0.8499	0.8634	0.8678	0.05	0.07
333	0.0976	0.0324	20.6	23.5	23.59	0.44	0.45	0.0694	0.0528	0.0324	0.91	1.60	0.1017	0.2016	0.2035	2.20	2.22
333	0.1001	0.0570	22.2	26.4	26.44	0.57	0.58	0.0712	0.0489	0.0570	1.24	0.51	0.1700	0.3053	0.3053	1.90	1.90
333	0.1013	0.0550	22.1	26.2	26.19	0.56	0.56	0.0710	0.0497	0.0550	1.18	0.34	0.1617	0.2980	0.2977	1.98	1.97
333	0.1053	0.1345	27.7	34.2	34.11	0.70	0.69	0.0654	0.0413	0.1345	1.50	3.53	0.3598	0.5030	0.4991	1.11	1.08
333	0.1103	0.2147	33.7	40.9	40.76	0.64	0.63	0.0540	0.0375	0.2147	1.20	4.68	0.5078	0.6163	0.6136	0.64	0.63

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